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CHEMICAL COMPOSITION OF THE EARTH'S MANTLE VIEWED AS THE SYSTEM : $\text{MgO-SiO}_2\text{-MgSiO}_3\text{-}$ Mg_2SiO_4

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CHEMICAL COMPOSITION OF THE EARTH'S MANTLE VIEWED AS THE SYSTEM: $\text{MgO-SiO}_2\text{-MgSiO}_3\text{-Mg}_2\text{SiO}_4$

BY

Mitsuhiko SHIMADA

1. Chemical equilibrium condition under the earth's gravitational field

Let us consider a system containing $j+1$ components under the earth's gravitational field. The chemical potential μ_i of the i -th component is regarded as a function of the depth, temperature, pressure and the molar fraction in the system. Equilibrium conditions can be written as follows:

$$d\mu_i = 0 = \left(\frac{\partial \mu_i}{\partial h}\right)_{TPx} dh + \left(\frac{\partial \mu_i}{\partial T}\right)_{hPx} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{hTx} dP + \sum_j \left(\frac{\partial \mu_i}{\partial x_j}\right)_{hTPx_{j-1}} dx_j, \quad (1)$$

where h , T , P and x_j are the depth from the surface, temperature, pressure and the molar fraction of the j -th component, respectively. There are only j independent variables, even though there are $j+1$ components, since the sum of all the molar fractions is maintained equal to unity. Constancy of x in the first three partial derivatives means that molar fractions of all components are kept constant. x_{j-1} in the partial derivative following the summation indicates that $j-1$ molar fractions are kept constant during each partial variation. Thermodynamical identities give

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{hPx} = -S_i, \quad (2)$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{hTx} = V_i, \quad (3)$$

and

$$\left(\frac{\partial \mu_i}{\partial h}\right)_{TPx} = -M_i g, \quad (4)$$

where S_i , V_i and M_i are the partial molar entropy, the partial molar volume and the molar weight of the i -th component, respectively, and g is the acceleration of gravity. If we assume the hydrostatic equilibrium to be maintained in the earth's mantle, we get

$$dp = \rho g dh, \quad (5)$$

where ρ is the mean density of the system.

If the system obeys Henry's law, then the chemical potential of the i -th component can be written as follows:

$$\mu_i = \mu_i^0 + RT \ln x_i, \quad (6)$$

where μ_i^0 is the chemical potential of a standard state of fixed T and P , and R is the gas constant.

Then we get from eqs. (1)–(6)

$$\frac{d \ln x_i}{dh} + \sum_{i \neq j} \left(\frac{\partial \ln \mu_i}{\partial x_j} \right)_{hTPx_{j-1}} \frac{dx_j}{dh} = -(\rho V_i - M_i) \frac{g}{RT} + \frac{S_i}{RT} \frac{dT}{dh}. \quad (7)$$

Brewer (1951) applied eq. (7) to the system: U–O₂–Si–Mg, and Shimazu (1955) to the system: FeO–Fe–SiO₂. They neglected the term of the temperature variation because of the small temperature gradient except close to the surface of the earth in Brewer's calculation and because of the small effect of temperature in Shimazu's. Let us roughly compare the two terms in the right hand side of eq. (7) to examine whether the constant temperature assumption is reasonable or not. The values of $(S_i dT/dh)/\{(\rho V_i - M_i)g\}$ for several materials are estimated as follows: 10^{-1} for Fe, 1.3×10^{-1} for Si, 2.3×10^{-1} for FeO and 1.4×10^{-1} for SiO₂. In estimating the values, we used $\rho = 4$ gm/cm³, $g = 10^3$ cm/sec² and $dT/dh = 1$ deg/Km and V_i , M_i and S_i were obtained from the tables of constants (e.g. Birch, et al., 1942). The results of this estimation show that the temperature term is not so small enough to be negligible.

To deal with chemical potential quantitatively we must use eq. (6) which is represented in terms of molar fraction, but owing to the definition of molar fraction we can discuss only the relative variation of materials at the fixed h , T and P .

2. The system: MgO–SiO₂–MgSiO₃–Mg₂SiO₄

It has been considered that the earth's mantle mainly consists of olivine ((Mg, Fe)₂ SiO₄). In this paper the system containing Fe is neglected. We consider the model of the earth's mantle composed of MgO, SiO₂, MgSiO₃ and Mg₂SiO₄.

Four chemical reactions written below are assumed to occur within this four-component system.



and



where each ΔG_k ($k=1, 2, 3$ and 4) is the Gibbs free energy change during the cor-

responding chemical reaction from left to right. Let $i=1=\text{MgO}$, $2=\text{SiO}_2$, $3=\text{MgSiO}_3$, and $4=\text{Mg}_2\text{SiO}_4$ (dependent component) in eq. (7). Observe that chemical potential is the partial molar Gibbs free energy, so that eq. (7) becomes (cf. Shimazu, 1956)

$$\left. \begin{aligned} \frac{1}{x_1} \frac{dx_1}{dh} + \frac{1}{RT} \cdot \frac{3\Delta G_1 + 2\Delta G_3}{2} \cdot \frac{dx_2}{dh} + \frac{1}{RT} \cdot 3\Delta G_2 \cdot \frac{dx_3}{dh} \\ = -(\rho V_1 - M_1) \frac{g}{RT} + \frac{S_1}{RT} \frac{dT}{dh} \quad (\text{for MgO}), \\ \frac{1}{x_2} \frac{dx_2}{dh} + \frac{1}{RT} \cdot \frac{3\Delta G_1 + 2\Delta G_3}{2} \cdot \frac{dx_1}{dh} \\ = -(\rho V_2 - M_2) \frac{g}{RT} + \frac{S_2}{RT} \frac{dT}{dh} \quad (\text{for SiO}_2), \\ \frac{1}{x_3} \frac{dx_3}{dh} + \frac{1}{RT} \cdot 3\Delta G_2 \cdot \frac{dx_1}{dh} \\ = -(\rho V_3 - M_3) \frac{g}{RT} + \frac{S_3}{RT} \frac{dT}{dh} \quad (\text{for MgSiO}_3), \\ x_4 = 1 - (x_1 + x_2 + x_3) \quad (\text{for Mg}_2\text{SiO}_4). \end{aligned} \right\} \quad (12)$$

To solve the molar fractions as functions of depth, h from eq. (12), all the coefficients must be written as functions of h . The distributions of density ρ , pressure P and gravity g are shown in Fig. 1 after Bullen (e.g. Birch et al., 1942). There are several theories as to the temperature distribution in the earth's mantle. The distributions based on adiabatic gradient (Verhoogen, 1951) and on melting point gradient (Uffen, 1952) indicate the minimum and the maximum distributions in the earth's mantle, respectively, then their mean distribution is used, though in the shallower depth than $h=200\text{Km}$ Gutenberg's (1951) is used. The result is shown in Fig. 2.

According to the theory of

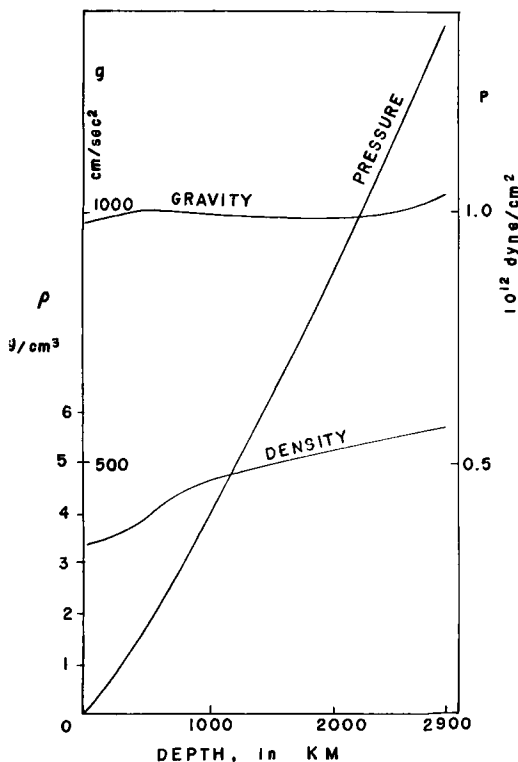


Fig. 1 Density, Pressure and Acceleration within the earth's mantle.

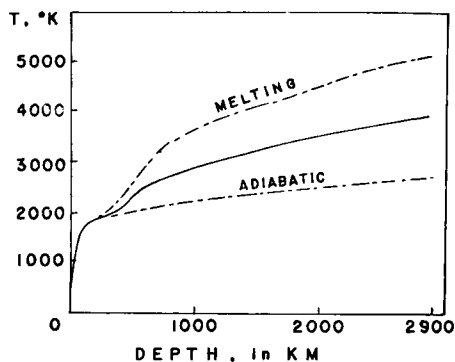


Fig. 2 Temperature within the mantle.

finite elastic strain (Birch, 1952),

$$V_0 = V(1+2f)^{3/2}, \quad (13)$$

$$P/K_0 = 3f(1+2f)^{5/2}, \quad (14)$$

where f is negative strain and V_0 and K_0 are the volume and the isothermal incompressibility at $P=0$, respectively. From eqs. (13) and (14) and the pressure distribution, f and V can be calculated as functions of depth and are given in Table 1.

Table 1 Negative strain f and molar volume V .

h, Km	f				$V(\text{cm}^3/\text{mol})$			
	MgO	SiO ₂	MgSiO ₃	Mg ₂ SiO ₄	MgO	SiO ₂	MgSiO ₃	Mg ₂ SiO ₄
0	0.0000	0.0000	0.0000	0.0000	11.23	22.64	31.50	43.80
33	0.0018	0.0065	0.0035	0.0024	11.17	22.21	31.17	43.49
200	0.0118	0.0465	0.0283	0.0159	10.84	19.79	29.00	41.79
400	0.0238	0.0833	0.0540	0.0309	10.47	17.60	27.01	40.03
600	0.0353	0.1142	0.0764	0.0451	10.14	16.63	25.45	38.48
1000	0.0589	0.1700	0.1178	0.0733	9.50	14.60	22.94	35.65
1400	0.0800	0.2149	0.1523	0.0978	8.99	13.24	21.04	33.50
2200	0.1163	0.2874	0.2098	0.1408	8.21	11.46	18.62	30.19

The Gibbs free energy change ΔG is obtained as a function of depth as follows (see Shimazu, 1958). The enthalpy change ΔH and ΔG_0 (ΔG at $P=0$) can be calculated from the integration of

$$\frac{\partial(\Delta H)}{\partial T} = \Delta C_p, \quad (15)$$

and

$$\frac{\partial}{\partial T} \left(\frac{\Delta G_0}{T} \right) = - \frac{\Delta H}{T^2}, \quad (16)$$

where C_p is specific heat at constant pressure. Specific heat C_p is known experimentally as a function of temperature, so ΔC_p can be obtained as the specific heat change during the chemical reaction from left to right. Then,

$$\Delta C_p = A + BT + CT^{-2}, \quad (17)$$

where A , B and C are constants. From eqs. (15), (16) and (17) we obtain

$$\Delta G^\circ = \Delta H^\circ - AT \ln T - \frac{B}{2} T^2 - \frac{C}{2} T^{-1} + kT, \quad (18)$$

where ΔH° and k are the constants of integration and can be obtained from

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad (19)$$

C_p , ΔH° and ΔS° are obtained from thermochemical tables (Birch, et al. 1942; Kubachewski and Evans, 1956; MacDonald).

For the reaction (8)

$$\Delta G^\circ_1 = -8.41 \times 10^3 + 0.04 T \ln T - 0.53 \times 10^{-3} T^2 + 2.40 \times 10^5 T^{-1} + 0.15 T,$$

for the reaction (9)

$$\Delta G^\circ_2 = -6.69 \times 10^3 - 0.88 T \ln T + 0.04 \times 10^{-3} T^2 + 0.43 \times 10^5 T^{-1} + 4.48 T,$$

for the reaction (10)

$$\Delta G^\circ_3 = -15.10 \times 10^3 - 0.84 T \ln T - 0.49 \times 10^{-3} T^2 + 2.83 \times 10^5 T^{-1} + 4.99 T,$$

for the reaction (11)

$$\Delta G^\circ_4 = -1.72 \times 10^3 + 0.92 T \ln T - 0.57 \times 10^{-3} T^2 + 1.97 \times 10^5 T^{-1} - 4.69 T,$$

in cal/mol.

(20)

Since the experimental data of C_p are restricted to a rather narrow range of temperature, the results for higher temperature are not so accurate. To obtain the Gibbs free energy change as a function of temperature and pressure, we assume

$$\Delta G = \Delta G_0 + P\Delta V, \quad (21)$$

though in this equation the effect of pressure on internal energy is neglected. From Fig. 1, Table 1, eqs. (20) and (21) we can obtain the Gibbs free energy change as a function of depth, and show it in Table 2.

Table 2 ΔG , in 10^{10} erg/mol.

h, Km	ΔG_1	ΔG_2	ΔG_3	ΔG_4
33	- 36.60	- 31.80	- 68.04	- 4.81
200	- 49.50	- 28.70	- 77.56	- 20.75
400	- 54.91	- 9.07	- 63.98	- 45.84
600	- 71.98	+ 13.12	- 58.85	- 85.10
1000	- 93.98	+ 73.34	- 20.64	-167.32
1400	-120.12	+144.96	+ 24.85	-265.08
2200	-160.34	+270.40	+110.06	-430.74

Finally entropy is obtained as follows.

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + P \left(\frac{\partial S}{\partial T} \right)_P dT. \quad (22)$$

Where

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V, \quad (23)$$

where α is thermal expansion, obtained from Grüneisen's ratio γ ,

$$\gamma = \frac{\alpha K_T / \rho}{C_v}. \quad (24)$$

γ is calculated from the theory of finite strain (Birch, 1952),

$$\gamma = -\frac{1}{6} + \left(\frac{\partial K_T}{\partial P}\right)_T, \quad (25)$$

$$\left(\frac{\partial K_T}{\partial P}\right)_T = \frac{12 + 49f}{3(1 + 7f)}, \quad (26)$$

$$\frac{K_T}{\rho} = \frac{K_{T_0}}{\rho_0}(1 + 2f)(1 + 7f), \quad (27)$$

where K_{T_0} is K_T (isothermal incompressibility) at $P=0$, $\rho_0=\rho$ (at $P=0$), and C_v is specific heat at constant volume and taken equal to $3R$. And

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}. \quad (28)$$

If we neglect the effect of pressure on C_p , we can obtain entropy as a function of depth from eqs. (22)–(28), Fig. 1 and Table 1, and the result is shown in Table 3.

Table 3 Entropy S , in 10^7 erg/deg mol.

h , Km	MgO	SiO ₂	MgSiO ₃	Mg ₂ SiO ₄
0	27.20	41.84	67.78	95.19
33	80.44	119.10	191.45	274.98
200	112.00	159.88	269.49	388.98
400	116.19	163.97	280.93	407.21
600	125.45	175.38	305.17	443.18
1000	133.01	182.38	326.73	476.07
1400	136.12	186.12	336.95	492.07
2200	142.04	193.71	356.12	521.32

3. Concluding remarks

Since the initial distribution of four components in the system is not known, we assume it to be in the same ratio by weight at $h=33$ Km. The solutions of eq. (12) under this assumption are shown in Fig. 3, (a) by molar fraction and (b) by percent by weight. Fig. 3 shows that in the deeper parts than a few hundred kilometers depth, MgSiO₃ is predominant.

The effect of pressure on the equilibrium temperature T_{eq} is given by Clapeyron-Clausius equation :

$$dT_{eq}/dp = \Delta V / \Delta S. \quad (29)$$

The result calculated from eq. (29), Table 1 and 3 for the chemical reactions (8), (9), (10) and (11), are shown in Fig. 4 with the temperature distributions (cf. Fig. 2).

The results are not discussed here further, for the accurate physical and chemical data under high temperature and pressure and the accurate initial data (at $P=0$)

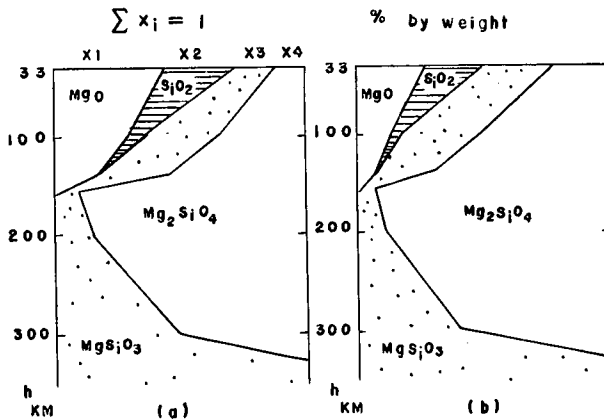


Fig. 3 Distribution of components as a function of depth, (a) by molar fraction and (b) by percent by weight.

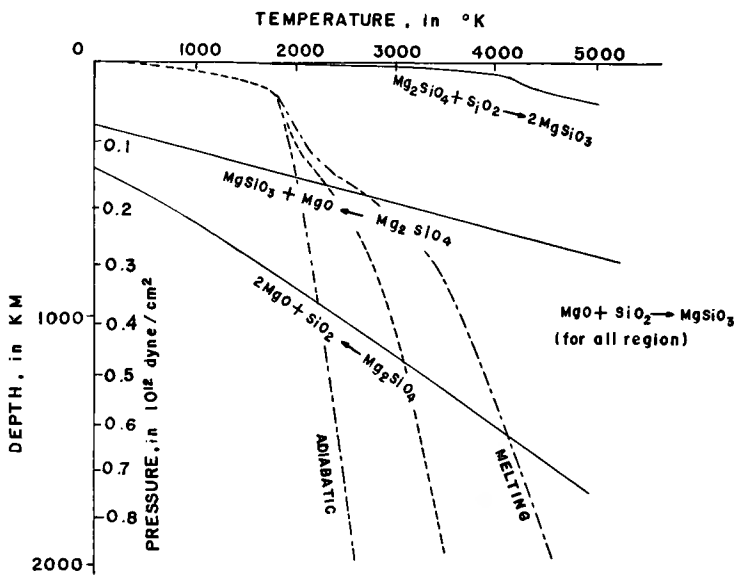


Fig. 4 Distribution of temperature of chemical equilibrium

are not available though many assumptions and neglections are used in this paper. We have been satisfied with only showing the method of calculation for the present.

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